Report 3

State of California
The Resources Agency
DEPARTMENT OF FISH AND GAME

Environmental Monitoring for Chemical Control of *Egeria densa* in the Sacramento-San Joaquin Delta, 1998

Office of Spill Prevention and Response
December 1998

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Environmental Monitoring for Chemical Control *of Egeria densa* in the Sacramento/San Joaquin Delta, 1998

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SUMMARY

In 1998, the California Department of Boating and Waterways began pilot treatments in several areas of the Delta with the copper-based aquatic herbicide. Komeen® to control the exotic aquatic weed Brazilian elodea *Egeria densa.*

Samples of water and sediment from Komeen®-treated areas were analyzed for total copper. Samples of water were tested for toxicity with fathead minnows *Pimephales promelas* and cladocerans *Ceriodaphnia dubia* to characterize conditions at Komeen ®-treated sites. Additionally, toxicity tests were conducted on Komeen® with the delta smelt *Hypomesus transpacificus.*

Copper concentrations in water samples from Komeen®-treated areas were highest at 3 hours posttreatment (mean concentration, 738 µg/L in Sandmound Slough, 461 µg/L in Sevenmile Slough, and 476 µg/L in White Slough). These concentrations generally declined to levels at, or near, the minimum detection limit of 50 µg/L within 24 hours. Water samples collected from treated sites 3 hours posttreatment produced significant mortality of cladocerans in 96-h acute toxicity tests, which appeared related to copper concentrations. The tests revealed that Komeen® toxicity dissipated partially within 24 hours after treatment. Water from Komeen®-treated sites produced variable mortality to fathead minnows. Toxicity of Komeen to delta smelt produced 96-h LC_{50} values of 24,400 µg/L and 14,995 µg/L (as Cu) in Sacramento River water and San Joaquin River water, respectively. In comparison, the toxicity (96-h LC_{50} values) of Komeen® to cladocerans and fathead minnows is approximately 110 µg/L and 4,668 µg/L (as Cu), respectively. Thus, the Korneen® applications for control of Brazilian elodea should have minimal impact to fish, especially delta smelt, but may have transient impacts on aquatic invertebrates, especially zooplankton. Komeen®-treated sites did not have higher sediment copper concentrations than did the control site. Similar impacts of Komeen® from the control of hydrilla have been documented in Clear Lake.

It is recommended that future monitoring of Komeen® applications concentrate on the measurement of copper concentrations in water, biota, and sediment. Furthermore, monitoring of toxicity to cladocerans and fish may be valuable.

INTRODUCTION

Introduced exotic aquatic plants have inhabited the California Sacramento-San Joaquin Delta for many years. However, mats of Brazilian elodea *Egeria densa* have now expanded to impair several beneficial uses of Delta waters. On January 1, 1997, Assembly Bill 2193 appointed Department of Boating and Waterways (DBW) as the lead agency in establishing an *Egeria* Control Plan (ECP) for the Delta and its tributaries. Brazilian elodea is an introduced aquatic plant that reproduces vegetatively, and it grows in water one to three meters deep in monoculture mats throughout the Sacramento-San Joaqum Delta. DBW estimates approximately 25 tons or more of Brazilian elodea (wet weight) per acre.

DBW selected three areas to compare mechanical and chemical control methods. DBW used the copper-based herbicide Komeen® to control Brazilian elodea in Sand Mound Slough, Sevenmile Slough, and White Slough in June 1998 (Figure 1). Komeen® is registered by the United States Environmental Protection Agency and the California Department of Pesticide Registration for the control of aquatic weeds including Brazilian elodea. Komeen® (complexed copper was applied at 750 ppb Cu adjacent to mechanical harvester sites. This allowed for a direct comparison between chemical and mechanical methods. Trial applications of Komeen ® provided essential information on efficacy and potential for environmental impacts. Monitoring data will be used in an environmental assessment of Brazilian elodea control strategies. DBW is drafting an environmental impact report for the long-term control of Brazilian elodea in the Delta.

The toxicity and environmental fate of copper in aquatic systems has been well documented. Copper is generally only biologically available for toxic effects in the ionic or dissolved form. The bioavailability of copper generally decreases with increasing water hardness, alkalinity, pH and turbidity (Erickson *et al.* 1996). In comparison to inorganic copper, the toxicity of the chelated ethylenediamine complex of copper in Komeen® to fish and other aquatic organisms has received lesser study. A previous study of the toxicity of Komeen® to aquatic organisms (Nelson *et al.* 1984) indicated that the use of the herbicide to eradicate hydrilla in California's Imperial Valley would provide limited margins of safety under local conditions, and that fish losses may occur if the fish were stressed by low dissolved oxygen concentrations or high water temperatures. The study also indicated that Komeen® was significantly more toxic to channel catfish *Icralurus punctatus* fry (96-h LC_{50} value = 18,100

µg/L) than to the juvenile life stage (96-h LCSQ = 46,400 µg/L). Toxicity tests on Komeen® performed by the Department of Fish and Game (Trumbo 1997) in Clear Lake water (hardness =100 to 150 mg/L $CaCO_3$) indicated that the 96-h LC_{50} value for larval fathead minnow *Pimephales promelas* was 4,668 µg/L (as Cu). The chelated form of copper in Komeen® appears to be at least one order of magnitude less toxic to fathead minnow than is inorganic copper (96-h LC_{50} values 170 to 260 ~±g[L) for water of similar hardness.

With respect to aquatic invertebrates, there is little data available in the literature that directly addresses Komeen® toxicity. Mayer and Ellersick (1986) reported that the 96-h LC50 value for apple sifail *Pomacea* sp. exposed to Komeen® was 52 µg/L (as Cu). Toxicity tests on Komeen® (Trumbo 1997) using Clear Lake water (hardness 100 to 150 mg/L $CaCO_3$) indicated that the 96-h LC_{50} value for the cladoceran *Ceriodaphnia dubia* was 110 µg/L (as Cu). Additional tests conducted using Clear Lake water found the 96-h LC_{50} value for Komeen® to the amphipod *Hyalella azreca* was >1.277 mg/L. (as Cu); the 96-h LC50 values in Clear Lake water for Komeen® were 31.800 µg/L and 640 µg/L (as Cu) for crayfish *Procambarus clarkii* and snails *Phvsa* sp., respectively (Trumbo 1998).

The objective of this study was to assess the impacts of Komeen® use on the aquatic fauna of Delta. To accomplish this, conditions before and after treatment with Komeen® were compared to conditions in a control area. Komeen® was applied at concentrations of approximately 750 µg/L (as Cu). Samples of water and sediment were analyzed for copper concentrations. Toxicity tests on water samples were conducted with invertebrates and fish. Toxicity tests were also conducted on Komeen® with delta smelt *Hvpomesus transpacificus.*

MATERIALS AND METHODS

Study Design

Samples of water and sediment were collected from four sites. Three of these sites within Komeen®-treatment areas (Sand Mound Slough, Sevenmile Slough, and White Slough) and one site was in a non-treatment area (negative control site near Sevenmile Slough) which served as the study control (Figure 1). Site selection was based on relative similarity of aquatic habitat quality.

Samples were collected according to protocols established in a quality assurance project plan (QAPP) (California Department of Fish and Game 1998). Each sample was accompanied by a chain-of-custody form which documented the sequence of transfer from sample generation to analysis (Appendix A). Samples were collected in June and August to coincide with Komeen® application schedules (Table 1).

Water Quality

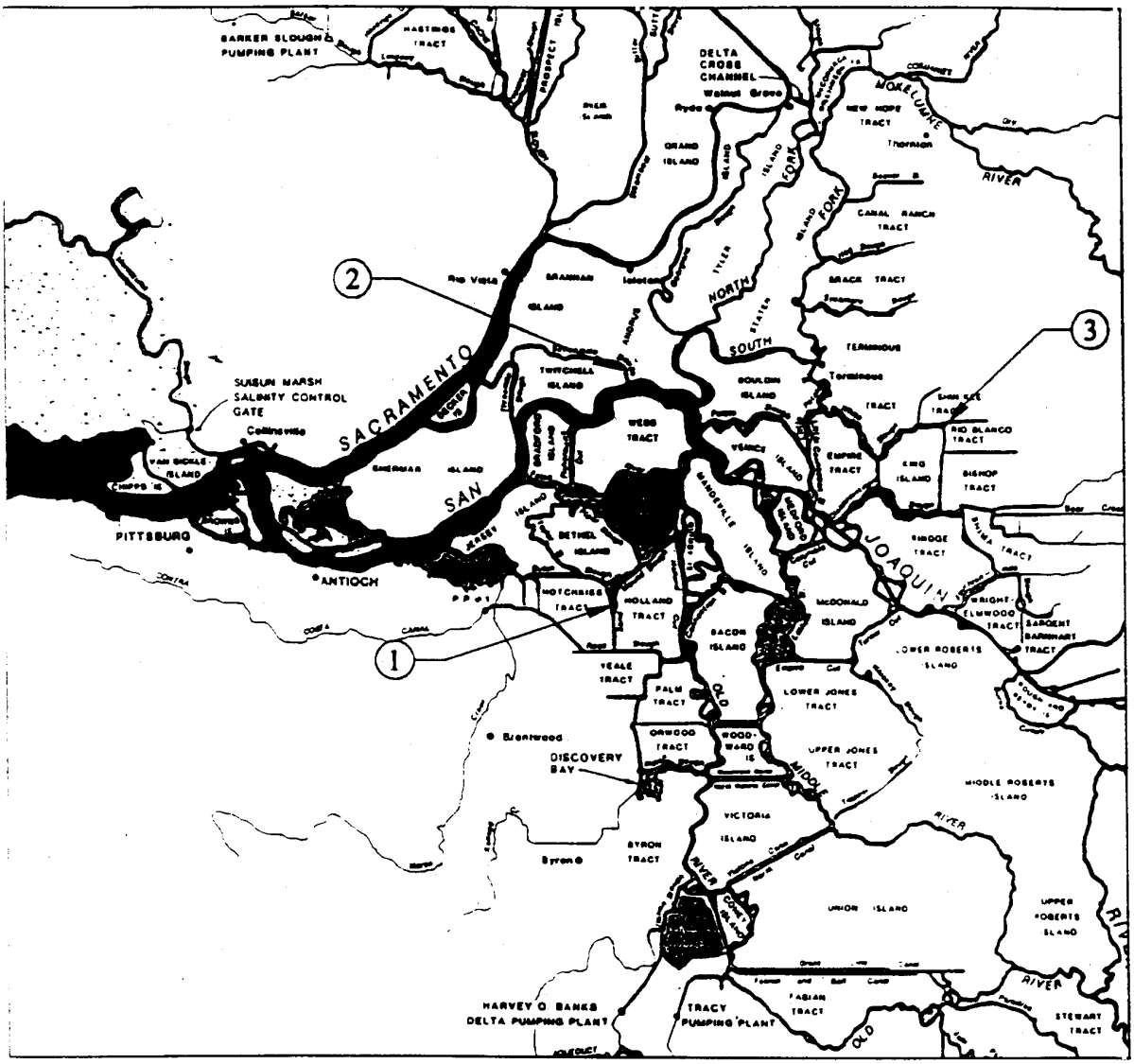
Sample Collection

Two or three sampling stations were sampled at each site. Stations #2 and #3 were within the treatment quadrat and Station #4 was outside of the treatment quadrat (Figure 2). Samples were collected at each station at two depths: (1) one foot below the surface and (2) one foot above the hydrosoil. Samples were decanted into chemically clean 250-mi high density polyethylene (HDPE) bottles and acidified with *0.5* ml of 6N nitric acid to pH 2. Samples were stored on wet ice at a temperature of 4^0C immediately after collection.

Sample collection was timed to coincide with Komeen® treatments according to the following schedule: (1) prior to treatment, (2) 3 hours posttreatment, (3) 9 hours posttreatment, and (4) 24 hours posttreatment.

Analysis

Copper concentrations in water were determined by flame atomic absorption spectrophotometry in USDA-ARS Aquatic Weed Laboratory.



1. Sand Mound Slough
2. Sevenmile Slough
3. White Slough

Figure 1. Komeen® treatment sites in Sacramento-San Joaquin Delta.

Table 1: Sampling and analyses schedule for monitoring in 1998.

Analysis	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar
Water Chemistry				*X*									
Sediment Chemistry				*X*	*X*	*X*							
Toxicity Testing				*X*									

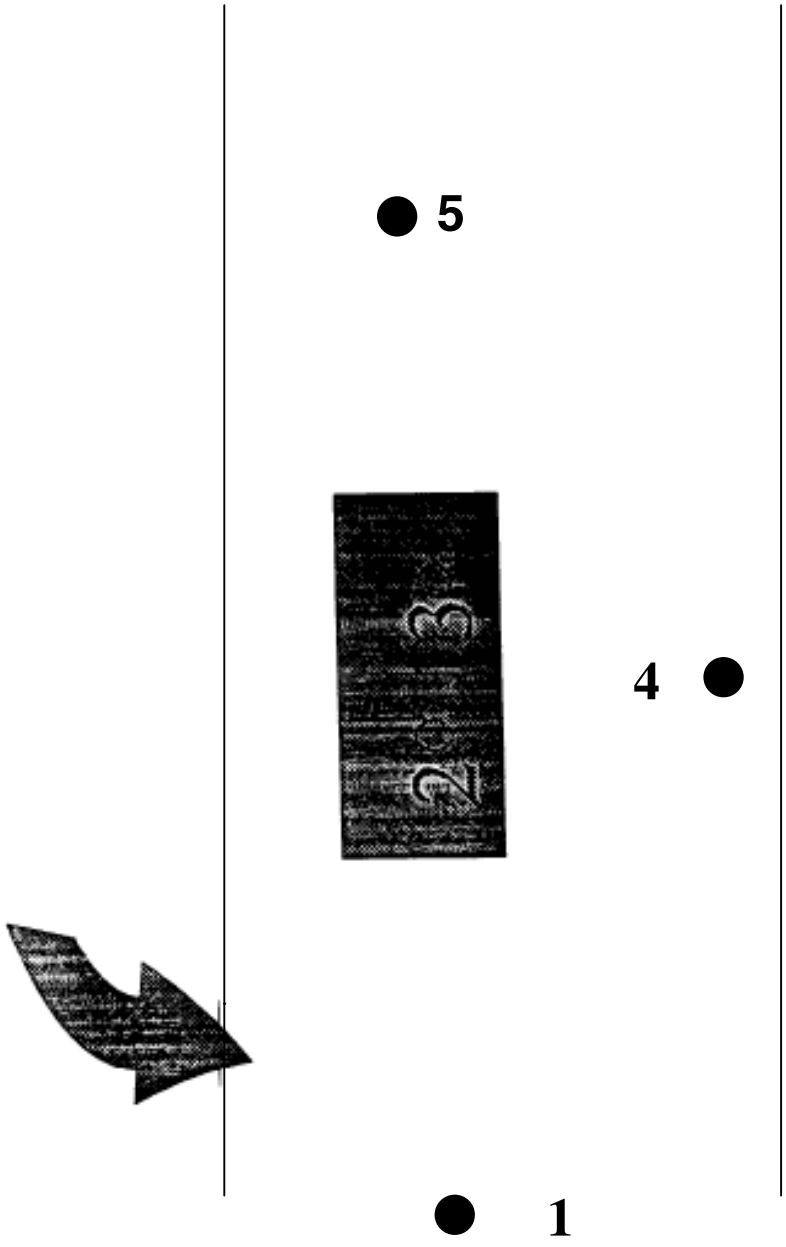


Figure 2. Sampling stations in relation to Komeen® treatment quadrant (shaded area).

Sediment Chemistry

Sample Collection

Sediment samples were collected prior to treatment, 30, and 60 days posttreatment. Five sampling stations were sampled at each site. Stations #2 and #3 were within the treatment quadrat and Stations #1, #4, and *#5* were outside of the treatment quadrat (Figure 2). The top six inches of hydrosoil was collected at each site using a core sampler lined with two-inch diameter acetate tubes. Approximately one pint of sediment was collected for each sample. Sample integrity was maintained by keeping the samples in the acetate liners and capping both ends. The top six inches of each sample was stored on wet ice at a temperature of 4^0C immediately after collection. The samples were later frozen in the laboratory pending chemical analysis. Prior to analysis, the six-inch cores were homogenized.

Analysis

Copper concentrations were determined by the simultaneously extractable metals (SEM) method for analysis by flame atomic absorption spectrophotometrv. A CDFG methodology was employed (CDFG 1998). Sediment samples were prepared for analysis by drying overnight at a temperature of 95 to 105^0C to a constant weight. Then 0.25 to 0.50 g of dry sediment was placed into a polyethylene bottle with 100 ml of 1 N hydrochioric acid, and the mixture was shaken for two hours. The digestate was then filtered through a 0.45-µm filter under vacuum, and the filtrate was then transferred to a polyethylene bottle pending analysis.

Toxicity Tests

Water Sampling

Water samples from two or three sampling stations at each site were collected without acid preservation for 96-h acute toxicity tests. Stations #2 and #3 were within the treatment quadrat and Station #4 was outside of the treatment quadrat (Figure 2). Water samples were

collected with hand-held sump pump from two depths: (1) one foot below the surface and (2) one foot above the hydrosoil.

After collection, equal volumes of water from the two depths were composited into precleaned, one-gallon plastic containers. A total volume of 1 gallon was collected for each sample. Samples were stored and transported at a temperature of 4^0C on wet ice. Samples were split for Cu chemical analysis (CDFG, 1998). The toxicity tests were conducted within three days of sample collection.

Sample collection was timed to coincide with Komeen® treatments according to the following schedule: (1) prior to treatment, (2) 3 hours posttreatment, (3) 9 hours posttreatment, and (4) 24 hours posttreatment.

Cladoceran Test Procedures

Cladoceran *Ceriodaphnia dubia* neonates (<24-h old) were exposed to undiluted water samples in 96-h static tests with renewal at 48 hours. Well water from the Aquatic Toxicology Laboratory was used as a control (hardness = 132 to 140 mg/L $CaCO_3$ pH = 7.80 to 8.76). The whole sample test procedures were based on United States Environmental Protection Agency protocols (USEPA 1993). Test organisms were obtained from laboratory cultures maintained using USEPA procedures. Five cladocerans were placed into 30-mi plastic cups containing 20 ml of sample. Four replicates were used per treatment. The test was conducted in an environmental chamber at a constant temperature of 25^0C. The cladocerans were fed a 1:1 mixture of yeast-Cerophyll®-trout chow and algae *Selenastrum capricornurum* suspension prior to renewal of the test solution. The photoperiod was 16:8 h light:dark. Mortality and water quality characteristics were recorded daily. Death was defined as a lack of response to persistent prodding.

Fish Test Procedures

Fathead minnow *Pimephales promelas* larvae (1 to 14-d old) were exposed to undiluted water samples in 96-h static tests with renewal at 48 hours. Well water from the Aquatic Toxicology Laboratory was used as a control (hardness = 132 to 140 mg/L $CaCO_3$ pH = 7.80 to 8.76). The test procedures were based on USEPA protocols (USEPA 1993'). Test organisms

were obtained from a commercial vendor (Aquatic Biosystems, Fort Collins. CO) and were acclimated to laboratory conditions prior to testing. Ten larvae were placed into 1.0-L glass chambers, each containing 250 ml of sample. Two replicates were tested per treatment. The test was conducted in an environmental chamber at a constant temperature of 25^0C. Fathead minnows were fed with brine shrimp nauplii prior to water renewal. The photoperiod was 16:8 h light:dark. Mortality and water quality characteristics were recorded daily during each test.

Toxicity Tests on Komeen®

Delta smelt Hypomesus *transpacificus* larvae (1 to 10-d old) were obtained from the State Water Project's Fish Facility at Byron, California, which is managed by the University of California at Davis. Test organisms were acclimated to laboratory conditions and mortality and water qualitv measurements for acclimation tanks were recorded daily (Linberg *et al.* 1998). Toxicity tests on Komeen® were performed according to American Society of Testing and Materials (ASTM) standard Guides E729-88 and El 192-88. The tests were 96-h in duration and test solutions were renewed daily. Sacramento River water (hardness = 86 mg/L $CaCO_3$) and San Joaquin River water (hardness = 66 mg/L $CaCO_3$) were used as a diluent and a control. Five larvae were placed into 50-ml plastic chambers, each containing 40 ml of sample volume. The test was conducted in an environmental chamber at a constant temperature of 14^0C. Four replicates were tested per treatment. The photoperiod was 16:8 h light:dark. Mortality and water quality characteristics were recorded daily during each test.

RESULTS AND DISCUSSION

Copper Concentrations in Water

The quality control results for the water analysis were satisfactory. Spike recoveries were in a range of 100 to 102% (mean 101%), and the mean precision was 0% (calculated as the relative percent difference).

Copper concentrations detected in negative control site samples were below the reporting limit of 50 µg/L. Copper concentrations in samples taken prior to the first herbicide application (Day –3) in June were also below the reporting limit of 50 µg/L (Figures 3, 4 and 5).

There was a sharp increase in water copper concentrations (3 hours after the application of Komeen®) immediately following herbicide treatments (Figures 3, 4 and 5). For samples taken from Sand Mound Slough, copper concentrations detected in water samples were 1226.9 µg/L at station #2 and 247.7 µg/L at station #3, with a mean copper concentration of *738* µg/L. For samples taken from Sevenmile Slough, copper concentrations detected in water samples were 99.6 µg/L at station #2 and 821.9 µg/L at station #3, with a mean copper concentration of 461) µg/L. For samples taken from White Slough, copper concentrations detected in water samples were 164.3 µg/L at station #2 and 786.7 µg/L at station #3, with a mean copper concentration of 476 µg/L (see appendix B).

Copper concentrations detected in samples taken 24 hours posttreatment showed a marked decrease from those at 3 hours posttreatment. Copper concentrations in 24 hours posttreatment samples ranged from the reporting limit of 50 µg/L to 119 µg/L (see appendix B). For Sand Mound Slough, copper concentrations detected in water samples were 119.0 µg/L at station #2 and 117.5 µg/L at station #3, with a mean copper concentration of 118 µg/L. For Sevenmile Slough, copper concentrations detected in water samples were 61.9 µg/L at station #2 and 98.1 µg/L at station #3, with a mean copper concentration of 80 µg/L. For White Slough, copper concentrations detected in water samples were 69.1 µg/L at station #2 and 133.3 µg/L at station #3, with a mean copper concentration of 101 µg/L. This indicates that the elevated copper concentrations found in water at Komeen® treatment sites were transitory in nature and were rapidly diminished by various mechanisms, including dilution into surrounding waters.

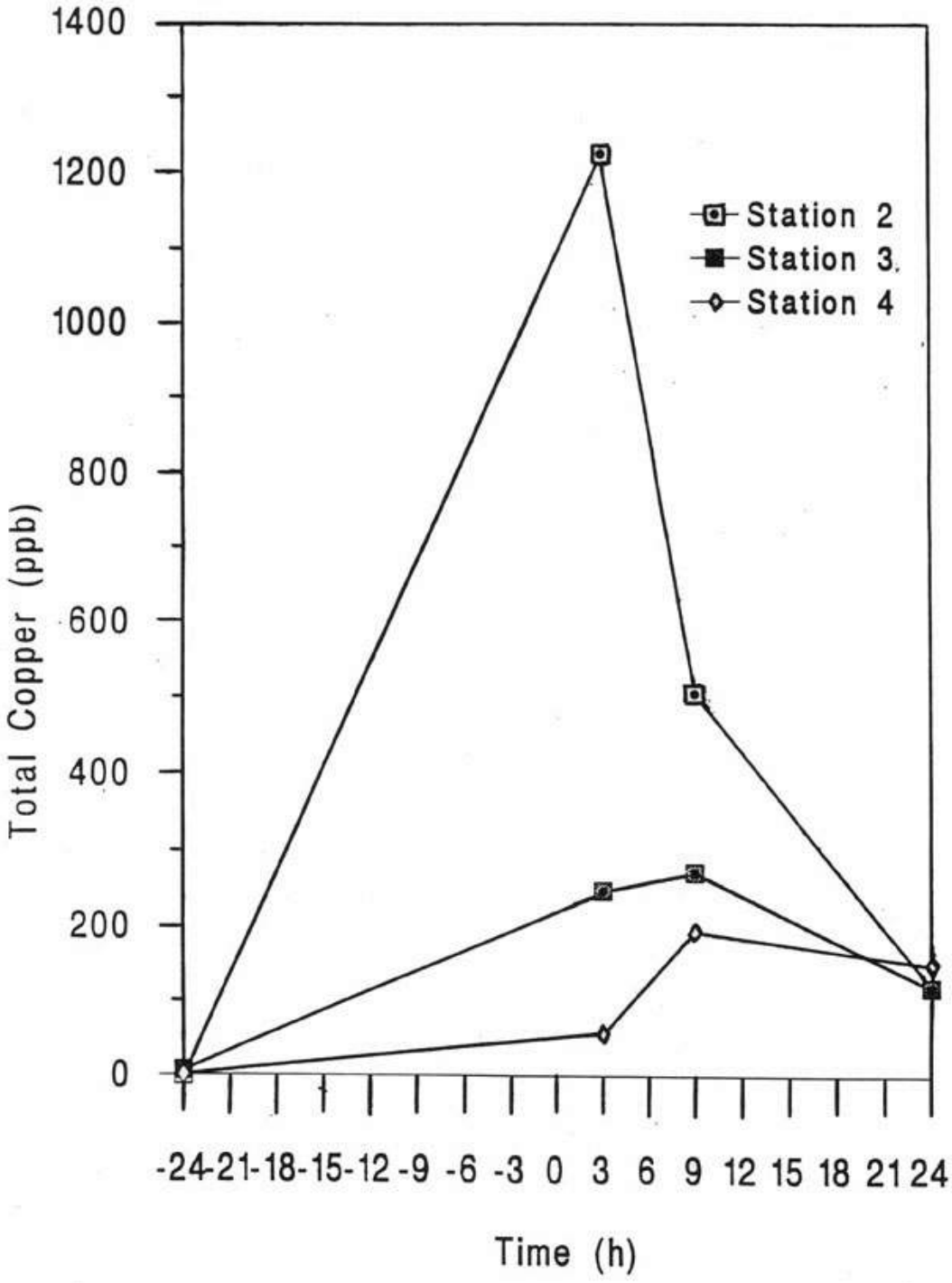


Figure 3. Mean Cu concentrations in water from surface and bottom of Sand Mound Slough.

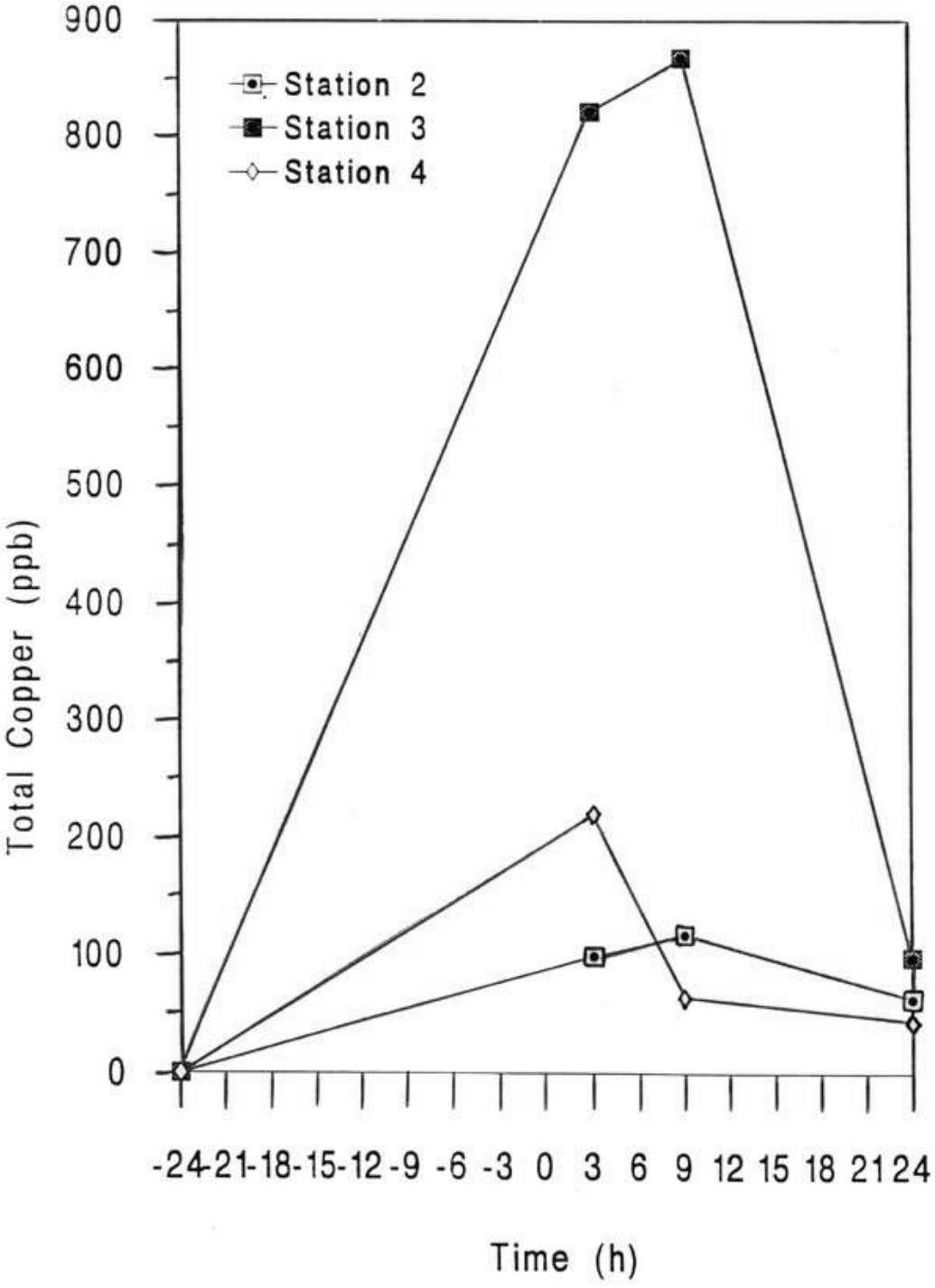


Figure 4. Mean Cu concentrations in water from surface and bottom of Sevenmile Slough (Owl Harbor).

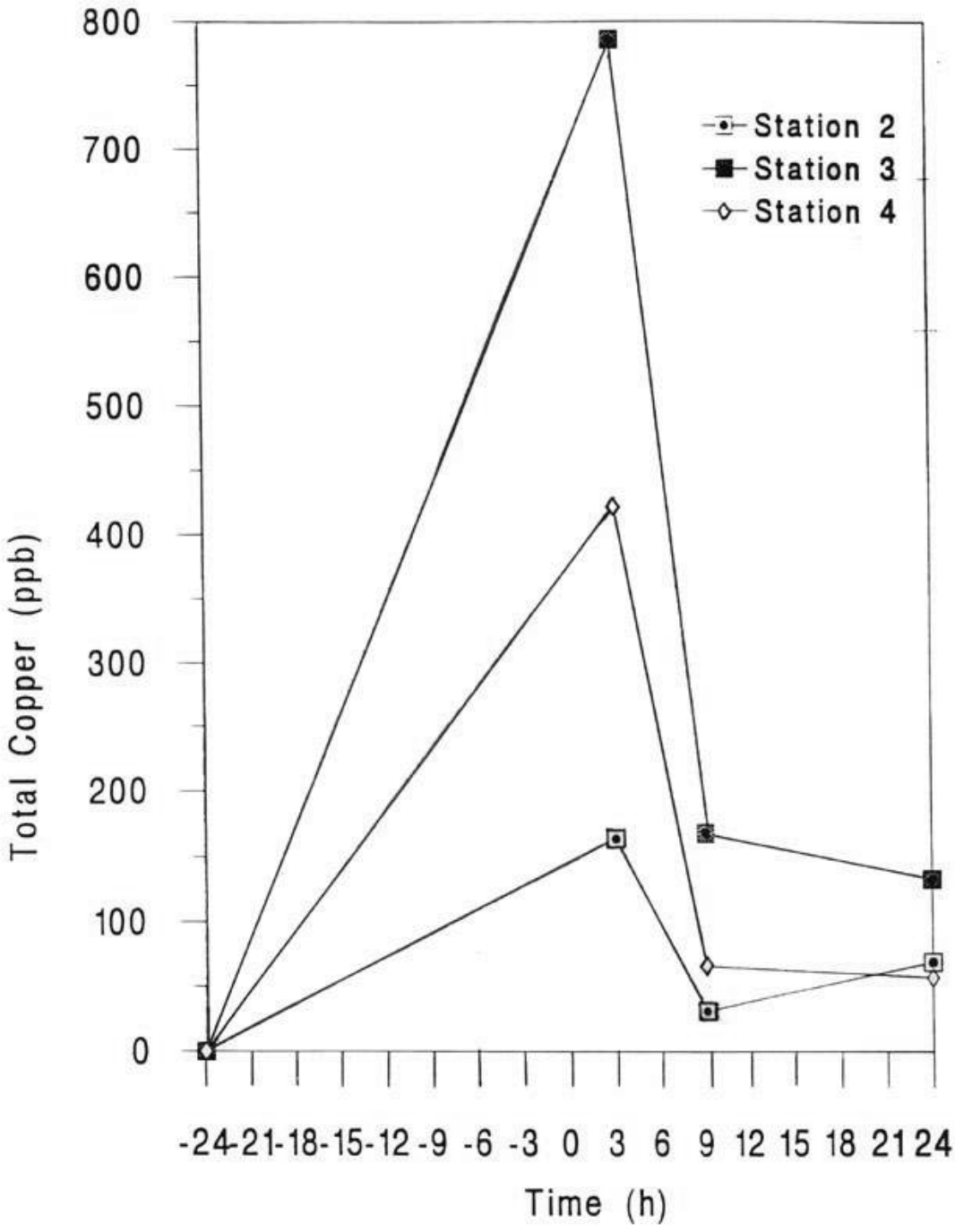


Figure 5. Mean Cu concentrations in water from surface and bottom of White Slough.

Copper Concentrations in Sediment

The quality control results for the analysis were satisfactory. Spike recoveries were in a Range of 93 to 100% (mean = *96.5%),* and the mean precision was 0%. Copper concentrations (expressed as dry wt.) detected in sediment during the project period ranged from the detection limit of 9 to 62µg/L.

Fifty-seven (57*)* sediment samples were collected. Control site samples contained copper residues in a range from 32 to 62 µg/g. There was very little variation in sediment copper concentrations at the control sites from June to September (Table 2). Copper concentrations in samples collected at Komeen®-treatment sites 30 day posttreatment were in a range from the detection limit of 9 µg/g to 102 µg/g. When the final samples were taken on 30 and 60 days posttreatment. Copper concentrations for all sites were at, or even lower than, the concentrations detected in samples collected before the first 1998 herbicide treatments. There was no significant difference in copper concentrations between pretreatment and posttreatment at Komeen® treatment sites (Table 2). However, the data did not lend itself to definitive conclusions regarding copper accumulation in sediment.

Table 2. Total copper concentrations (simultaneously extracted metals µg/g, dry wt.) in sediment before and after Komeen® treatment.

Site	Station 1	Station 2	Station 3	Station 4	Station 5
Pretreatment					
Negative Control	32	39	32	--	--
Sevenmile Slough (Owl Harbor)	62	41	52	48	36
White Slough	38	21	19	18	37
Sand Mound Slough	41	29	13	<RL	10
30 d posttreatment					
Negative Control	42	62	53	--	--
Sevenmile Slough (Owl Harbor)	66	33	34	32	59
White Slough	32	17	31	27	31
Sand Mound Slough	88	17	102	13	17
60 d posttreatment					
Negative Control	36	60	60	--	--
Sevenmile Slough (Owl Harbor)	40	34	43	45	40
White Slough	31	21	45	16	35
Sand Mound Slough	<RL	40	<RL	<RL	<RL

<RL indicates copper concentrations less than the reporting limit of 9 µg/g, dry wt.

Toxicity Tests

Thirty six (36) water samples were collected from June 12 through 20 for toxicity tests with cladocerans and fathead minnows.

Toxicity of Water to Cladocerans

The quality control results for the toxicity tests were considered good. Test organism response to a standard toxicant, sodium chioride (NaCl) was satisfactory. Standard toxicant responses during the test period were within 1.5 standard deviations of the test mean (LC_{50} = 1.88 g/L).

Tests performed with water samples collected prior to Komeen® treatment produced no significant mortality to *C. dubia* (Table *3).* Additionally, no significant mortality was seen at the negative control site.

Overall, water samples collected at treatment sites *3* hours posttreatment were very toxic to *C. dubia.* Complete mortality (survival of 0%) of the test organisms generally occurred in the undiluted sample waters from treatment sites. Water samples with significant mortality contained copper concentrations in a range of 150 to 800 µg/L (Table *3).* These copper levels were consistently higher than the 96-h $LC\sim_0$ value for cladocerans of 110 µg/L (as Cu) (Trumbo 1997). Simple correlation *P<0.05)* was used to examine the relationship between water copper concentrations and cladocerans survival. Survival (%) was negatively correlated with copper concentrations *(r* = 0.686. *P* < 0.05, Figure *5).* Thus, the mortality observed in the *3* hours posttreatment samples was expected and probably due to Komeen®. It appears that the sample collected in Station #2 at the Sevenmile treatment site on June 17 did not produce cladoceran mortality because the copper concentration in that sample was low *(50* µg/L). This sample was probably poorly mixed.

The toxicity caused by Komeen® generally dissipated within 24 hours. Tests performed on water samples taken 24 hours posttreatment produced 80 to 100% survival. There was less significant cladoceran mortality because copper concentrations by 24 hours posttreatment had dissipated to 100 µg/L or less; a concentration range that would not be expected to produce mortality (Table *3).*

Table 3. Water quality characteristics and 96-h toxicity of water samples from the Delta to fathead minnows and cladocerans.

Date	Time	Location	Total Alkalinity (mg/L $CaCO_3$)	Total Hardness (mg/L $CaCO_3$)	Specific Conductivity (µS/cm)	Cu conc. (µg/L)	Percent Survival: Fathead Minnows Control	Fathead Minnows Sample	Cladocerans Control	Cladocerans Sample
6/12	- 3d	White Slough #2	70	82	240	<RL	90	90	100	85
6/12	- 3d	White Slough #3	68	72	209	<RL	90	80	100	100
6/12	- 3d	White Slough #4	60	76	180	<RL	90	90	100	100
6/15	+ 3h	White Slough #2	88	98	270	410	100	80	100	0*
6/15	+ 3h	White Slough #3	78	82	227	300	100	90	100	0*
6/15	+ 3h	White Slough #4	74	80	219	150	100	95	100	40*
6/15	+ 9h	White Slough #2	82	90	259	70	100	100	100	90
6/15	+ 9h	White Slough #3	92	90	293	90	100	95	100	80
6/15	+ 9h	White Slough #4	88	98	303	100	100	90	100	50*
6/16	+ 24h	White Slough #2	88	90	273	<RL	100	100	100	95
6/16	+ 24h	White Slough #3	82	104	243	50	100	95	100	100
6/16	+ 24h	White Slough #4	82	92	244	<RL	100	100	100	70*
6/12	- 5d	Seven mile Slough #2	22	50	137	<RL	100	100	100	100
6/12	- 5d	Seven mile Slough #3	22	50	136	<RL	100	100	100	100
6/17	+ 3h	Seven mile Slough #2	44	60	143	50	100	100	100	90
6/17	+ 3h	Seven mile Slough #3	48	76	144	800	100	60*	100	0*
6/17	+ 9h	Seven mile Slough #2	42	54	142	<RL	100	90	100	20*
6/17	+ 9h	Seven mile Slough #3	38	58	145	<RL	100	75*	100	0*
6/18	+ 24h	Seven mile Slough #2	46	52	136	<RL	NA	NA	100	90
6/18	+ 24h	Seven mile Slough #3	42	56	145	100	NA	NA	100	30*
6/12	- 5d	Negative Control	44	50	130	<RL	100	100	100	95
6/17	+ 3h	Negative Control	42	52	126	<RL	100	100	100	100
6/17	+ 9h	Negative Control	40	46	125	<RL	100	95	100	95
6/18	+ 24h	Negative Control	42	50	128	<RL	NA	NA	100	100
6/12	- 7d	Sand Mound Slough #2	48	70	215	<RL	100	100	100	100
6/12	- 7d	Sand Mound Slough #3	46	62	224	<RL	100	100	100	95
6/12	- 7d	Sand Mound Slough #4	44	66	218	<RL	100	100	100	100
6/19	+ 3h	Sand Mound Slough #2	48	70	207	800	100	80	100	0*
6/19	+ 3h	Sand Mound Slough #3	48	80	212	430	100	70*	100	0*
6/19	+ 3h	Sand Mound Slough #4	46	62	205	<RL	100	93	100	100
6/19	+ 9h	Sand Mound Slough #2	44	60	209	180	100	85	100	0*
6/19	+ 9h	Sand Mound Slough #3	44	80	206	280	100	90	100	0*
6/19	+ 9h	Sand Mound Slough #4	44	80	207	170	100	75*	100	0*
6/20	+ 24h	Sand Mound Slough #2	46	70	195	70	NA	NA	100	80
6/20	+ 24h	Sand Mound Slough #3	46	60	199	80	NA	NA	100	90
6/20	+ 24h	Sand Mound Slough #4	44	60	190	100	NA	NA	100	55*

*: Survival signficantly less than the control group ($P < 0.05$).
<RL: less than reporting limit of 50 µg/L
NA: Test not available.

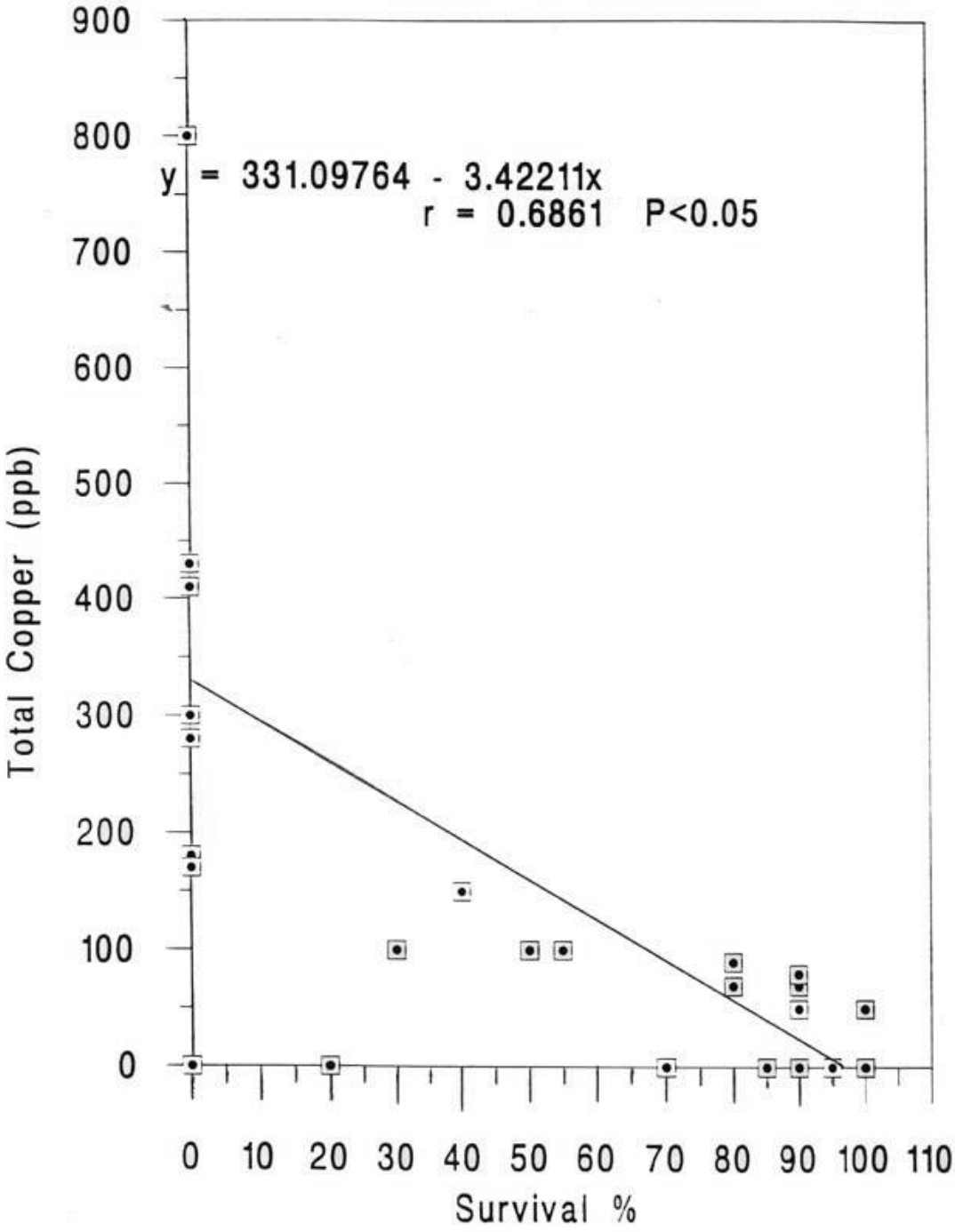


Fig. 6. The correlation of water copper concentration and cladocerans survival

In summary, exposure to Delta water collected immediately after Komeen® treatment resulted in complete mortality to cladocerans in laboratory toxicity tests. This mortality was mostly removed within 24 hours and appeared related to the copper concentration (Figure 6).

Toxicity of Water to Fathead Minnows

The quality control results for the water tests were considered good. The response to a standard toxicant potassium chloride (KCl) was satisfactory. Standard toxicant test response during the test period was within 1.5 standard deviations of the test mean (LC_{50} = 0.842 g/L).

Tests performed with water samples collected prior to Komeen® treatment produced no significant mortality to fathead minnows (Table 3). Additionally, no significant mortality was seen at the negative control site.

Water samples collected from Komeen®-treatment sites *3* hours posttreatment produced significant mortality with only two samples. Sample collected on June 17 at Sevenmile produced 60% survival and sample collected on June 19 at Sand Mound site produced 70% survival. Copper concentrations measured at these sites were 800 and 430 µg/L, respectively. The 96-h LC50 value established for larval fathead minnows using Clear Lake water was 4,668 µg/L (as Cu) (Trumbo 1997); mortality would generally first be observed at about half this concentration (the incipient lethal level or ILL) or about 2,300 µg/L (as Cu). However, Clear Lake water (110 to 150 mg/L $CaCO_3$) had higher hardness than Delta water (60 to 80 mg/L $CaCO_3$). The LC_{50} value of Komeen® (as Cu) in Delta water should be a out one-half that in Clear Lake water based in hardness. Thus, a ILL of 1,200 µg/L (as Cu) is possible. Samples collected 9 hours posttreatment at Sevenmile Slough site on June 17 and at Sand Mound site on June 19 produced mortality *(75%* survival). The mortality of fathead minnow larvae may be related to copper toxicity.

Definitive LC_{50} Toxicity Tests with Komeen® on delta smelt

The toxicity tests conducted on Komeen® produced a 96-h LC_{50} of 14.995 µg/L (as Cu) using water collected from San Joaquin River (Table 4). When water from Sacramento River was used a slightly higher 96-h LC_{50} value of 24,400 µg/L (as Cu) was produced. The difference in LC50 values is probably due to differences in hardness and pH. These values are two orders magnitude higher than the mean copper concentrations that were detected in water samples collected 3 hours after the application of Komeen®. Therefore, little direct mortality to delta smelt from the application of Komeen® far Brazilian elodea control would be expected.

Table 4. Results of toxicity tests (µg/L as Cu) on Komeen with larval delta smelt *Hypomesus transpacificus.*

SPECIES	96-H LC50	TEST RANGE	DILUTION WATER
Delta smelt	24,400	21,445 - 28,573	Sacramento River (86,7.85)
Delta smelt	14,995	11,447 – 19,733	San Joaquin River (66,7.29)

1) with hardness in mg/L $CaCO_3$ pH in parentheses.

SUMMARY AND RECOMMENDATIONS

Copper Concentrations in Water and Sediment

Copper concentrations in water were closely related to the use of Komeen®. Measured peak copper concentrations were within the expected range (461 to 738 µg/L) 3 hours posttreatment and dissipated to near background levels within 24 hours posttreatment.

Copper residues in sediment from Komeen®- treatment sites did not differ significantly from the control site. There was little evidence to suggest an accumulation of copper in sediment during the project period. The maximum copper residue found in sediment was 102 mg/g (dry wt). This is only about one-third of the reported effect range-median (ER-M) value of 390 mg/g for copper (Long and Morgan 1991). The ER-M is the concentration of a metal in sediment at which biological effects are frequently observed or predicted for most species (Kemble et al. 1994). Trumbo (1997, 1998) noted higher sediment copper concentrations in Komeen® treatment sites than control sites. Trumbo (1997) also found higher copper concentrations in the upper three inches of sediment than the next three inches (three to six). Thus, there may be a potential for copper to accumulate in sediment Komeen®- treated areas.

Recommendanons: Future treatments of Komeen® in Delta will probably result in copper concentrations in water and sediment similar to the levels measured in this study. Monitoring for copper residues, however, should continue because of concerns regarding the persistent nature, and possible accumulation over time, of the metal. The expected continuation of Komeen® use in Delta for several years also adds potential for copper to accumulate in sediment over time. Sediment sampling should be accompanied by water monitoring. In the future, consideration should be given to analyzing the upper levels of sediment and biota from the area for copper residues. If copper is found to accumulate in sediment, the toxicity tests on the sediment would be prudent.

Toxicity Tests with Water and Sediment

This study provided strong evidence that the application of Komeen® at rates necessary to control/eradicate *Egeria dansa* will produce significant mortality to sensitive aquatic invertebrates (cladocerans), but will produce less effect to fathead minnows. Komeen® rates used in the study will have minimun impact to delta smelt.

Recommendations: Impacts on the cladoceran species appears to be well-established. These toxicity tests should be continued in conjunction with monitoring of total copper concentrations in water and sediment to establish bioavailabilitv of copper at the site. Sediment toxicity tests should be undertaken if monitoring reveals an increase in sediment copper. No future toxicity testing of delta smelt and fathead minnows is needed.

Acknowledgments

We thank Dr. Joan Lindberg for supplying delta smelt larvae to toxicity tests. We also thank Chris Pirosko, Abdou Mekebri, and Matthew Zinki for copper analyses in water and sediment water samples. .

V. REFERENCES CITED

American Society for Testing and Materials (ASTM). 1994. Standard guide for conducting acute toxicity tests with fishes, macroinvertebrates and amphibians. Designation E729-88 and El 192188 in annual book of ASTM standards. Volume 11.04.

Erickson, R.J., D.A. Benoit, V.R. Mattson, Jr., and E.N. Leonard. 1996 The effects of water chemistry on the toxicity of copper to fathead minnows. Environmental Toxicology and Chemistry, 15:181-193.

California Department of Fish and Game. 1998. Quality assurance project plan for environmental monitoring of copper residues and toxicity in water and sediments from Sacramento-San Joaquin Delta, California. California Department of Fish and Game, Pesticide Investigations Unit, Rancho Cordova.

Kemble. N.E.. XV. G. Brumbaugh. E. L. Brunson, F. J. Dwyer. C. G. Ingersoll, D. P. Monda. and D. F. Woodward. 1994. Toxicity of metal-contaminated sediments from the Upper Clark Fork Rover, Montana. to aquatic invertebrates and fish in laboratory exposures. *Environmental Toxicology and Chemistry.* 13(12): 1985-1997.

Lindberg, J., R. Mager, B. Baskerville-Bridges, J. Kulczyk, J. Van Eenennaam, and S. Doroshov. 1998. Delta Smelt Culture, 1997. Department of Animal Science, University of California. Davis. CA.

Long, E. R. and L. G. Morgan. 1991. The potential for biological effects of sediment-sorbed contaminants tested in the National status and Trends Program. NOS OMA *52.* Technical Memorandum. National Oceanic and Atmospheric Administration, Seattle, WA. *cited in:* Kemble et aL, 1994.

Mayer, Foster L. Jr. Mark R. Ellersick. 1986. Manual of acute toxicity: Interpretation and database for 410 chemicals and 66 species of freshwater animals. USD1 Fish and Wildlife Service Resource Publication 160. Washington D.C.

Nelson. J.L., B.J. Finlavson, and T.S. Lew. 1984. Sensitivity of channel catfish to aquatic herbicides for hydrilla control and eradication in Imperial Valley, California. California Department of Fish and Game. Environmental Services Branch Administrative Report No. 84-2

Trumbo, J. 1997. Environmental monitoring of hydrilla eradication activites in Clear Lake, California Department of Fish and Game, Office of Spill Prevention and Response, Administrative Report 97-3, Sacramento, CA.

Trumbo, J. 1998. Environmental monitoring of hydrilla eradication activities in Clear Lake, California Department of Fish and Game, Office of Spill Prevention and Response, Administrative Report 98-3, Sacramento, CA.

United States Environmental Protection Agency. 1993. Methods for measuring the acute Toxicity of effluents and receiving waters to freshwater and marine organisms. Fourth Edition. EPA-600/4-90-027F. Cincinnati, Ohio.

Appendix A. California Department of Fish and Game, Pesticide Investigations Unit, Chain of Custody Form.

DFG REQUEST FOR ANALYSIS AND CHAIN OF CUSTODY RECORD

Page ____ of ____

SAMPLER PHONE #	SEND RESULTS TO	FOR LABORATORY USE ONLY LAB NUMBER
ADDRESS	ADDRESS	FIELD NUMBER
CITY CA ZIP	CITY CA ZIP	LAB STORAGE
DATE REQUIRED/REASON	COPIES TO	SPILL TITLE
SHIPPED VIA	ADDRESS	SUSPECT
	CITY STATE ZIP	INDEX-PCA

- ❑ Fish & Wildlife Loss Date:_____ Region: _____
- ❑ DFG Code Violation _____
- ❑ Suspected or Potential Problem
- ❑ Routine Analysis

Water Temp: °F or °C pH: DO: mg/L Conductivity: umhos/cm

ANALYSIS REQUESTED →

Sample Identification/Location (Draw Map on Separate Sheet If Necessary)	Collection Date	Collection Time	PETROLEUM FINGERPRINT	TRACE ELEMENTS (SPECIFY BELOW)	PESTICIDES (SPECIFY BELOW)							Sample Type: WATER	Sample Type: FILTERED WATER	Sample Type: SOIL	Sample Type: TISSUE		Number of Containers: PLASTIC	Number of Containers: GLASS	Number of Containers: VOA VIAL		Preservation: TEMP	Preservation: ACID

Problem Description

Suspect/Incident Location

Comments/Special Instructions

POLLUTION ACTION KIT REQUESTED: YES ❑ NO ❑

GLOVE SIZE: LARGE ❑ MEDIUM ❑

HAZMAT SHIPPER REQUESTED: YES ❑ NO ❑

SAMPLE(S) RELINQUISHED BY (SIGNATURE)	PRINT NAME	DATE	RECEIVED BY (SIGNATURE)	PRINT NAME

❑ Water Pollution Control Lab

FG 1000 (Rev. 11/94)

Appendix B. Mean Copper concentrations (µg/L) from two depths (surface and bottom) in water sample from June Komeen® treatment by USDA-ARS Aquatic Weed Lab.

Station	Sample Interval	Mean (n = 4)	S. D.	Mean btw #2 & #3
Sand Mound Slough				
# 2	Pretreatment	<RL	NA	NA
# 3	Pretreatment	<RL	NA	
# 4	Pretreatment	<RL	NA	
# 2	3 h posttreatment	1226.9	1045.5	738
# 3	3 h posttreatment	247.7	237.6	
# 4	3 h posttreatment	57.1	11.2	
# 2	9 h posttreatment	505.6	391.8	389
# 3	9 h posttreatment	272.9	292.0	
# 4	9 h posttreatment	194.2	155.8	
# 2	24 h posttreatment	119.0	34.6	118
# 3	24 h posttreatment	117.5	15.5	
# 4	24 h posttreatment	148.8	61.2	
Sevenmile Slough				
# 2	Pretreatment	<RL	NA	NA
# 3	Pretreatment	<RL	NA	
# 4	Pretreatment	<RL	NA	
# 2	3 h posttreatment	99.6	15.0	461
# 3	3 h posttreatment	821.9	10.0	
# 4	3 h posttreatment	220.7	206.2	
# 2	9 h posttreatment	117.3	118.7	493
# 3	9 h posttreatment	867.7	33.4	
# 4	9 h posttreatment	64.0	26.2	
# 2	24 h posttreatment	61.9	29.0	80
# 3	24 h posttreatment	98.1	0.7	
# 4	24 h posttreatment	<RL	<RL	

Station	Sample Interval	Mean (n = 4)	S. D.	Mean btw #2 & #3
White Slough				
# 2	Pretreatment	<RL	NA	NA
# 3	Pretreatment	<RL	NA	
# 4	Pretreatment	<RL	NA	
# 2	3 h posttreatment	164.3	187.1	476
# 3	3 h posttreatment	786.7	20.0	
# 4	3 h posttreatment	423.0	156.7	
# 2	9 h posttreatment	31.3	8.6	99
# 3	9 h posttreatment	167.6	34.2	
# 4	9 h posttreatment	66.7	19.6	
# 2	24 h posttreatment	69.1	0.7	101
# 3	24 h posttreatment	133.3	74.7	
# 4	24 h posttreatment	57.5	14.7	
Negative Control	Pretreatment	<RL	NA	
Negative Control	3 h posttreatment	<RL	NA	
Negative Control	9 h posttreatment	<RL	NA	
Negative Control	24 h posttreatment	<RL	NA	

RL: less than reporting limit of 50 µg/L

Appendix C. Mean Copper concentrations (µg/L) from water sample for toxicity testing from June Komeen® treatment by CDFG-Water Pollution Control Lab.

Station	Sample Interval	Cu conc.(µg/L)
Sand Mound Slough		
# 2	Pretreatment	<RL
# 3	Pretreatment	<RL
# 4	Pretreatment	<RL
# 2	3 h posttreatment	800
# 3	3 h posttreatment	430
# 4	3 h posttreatment	<RL
# 2	9 h posttreatment	180
# 3	9 h posttreatment	280
# 4	9 h posttreatment	170
# 2	24 h posttreatment	70
# 3	24 h posttreatment	80
# 4	24 h posttreatment	100
Sevenmile Slough		
# 2	Pretreatment	<RL
# 3	Pretreatment	<RL
# 2	3 h posttreatment	50
# 3	3 h posttreatment	800
# 2	9 h posttreatment	<RL
# 3	9 h posttreatment	<RL
# 2	24 h posttreatment	<RL
# 3	24 h posttreatment	100